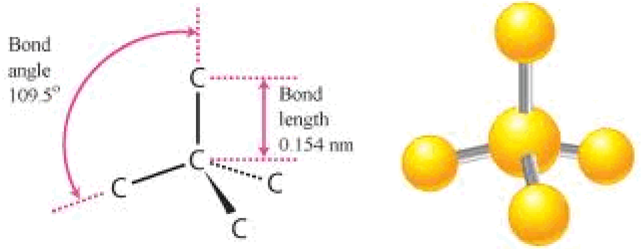
7. Carbon Nanostructures

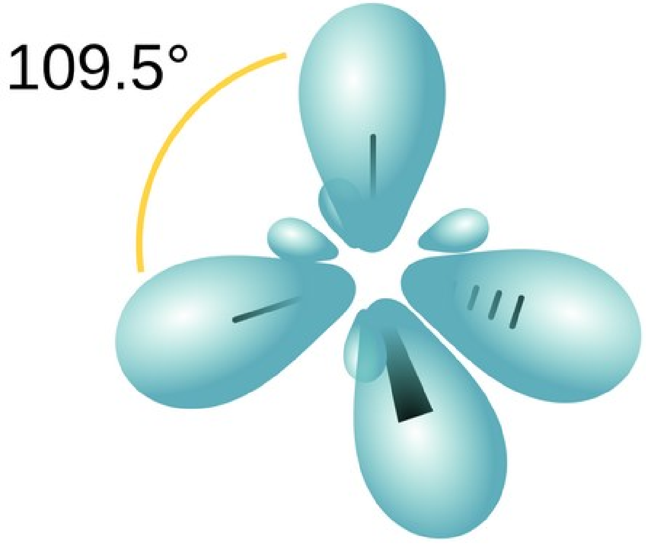
Repetition from the Last Lecture

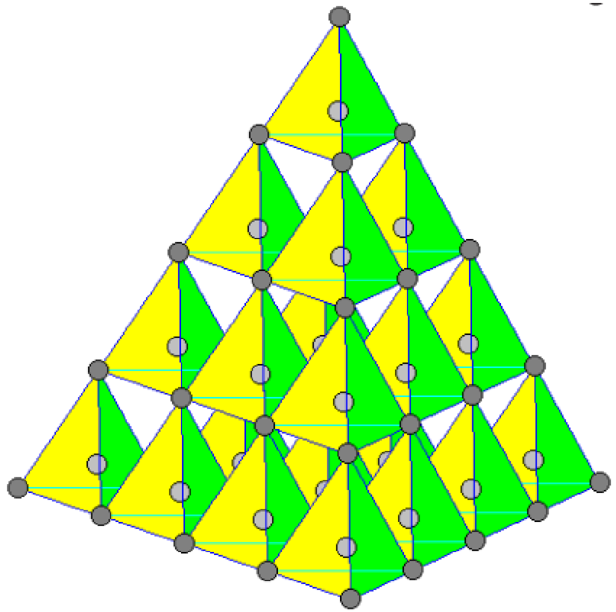
- Name the 3 basic steps of micromachining.
- List at least 3 techniques of NEMS fabrication.
- What forces are used by the NEMS gyroscope?
- Where is the MEMS component located in a DLP projector?
- List 3 basic fluid pumping options in microfluidic applications.

Carbon – Orbital Hybridisation

- **sp^3**
- 4 sp orbitals pointing to the corners of a regular tetrahedron
- Tetrahedral diamond structure

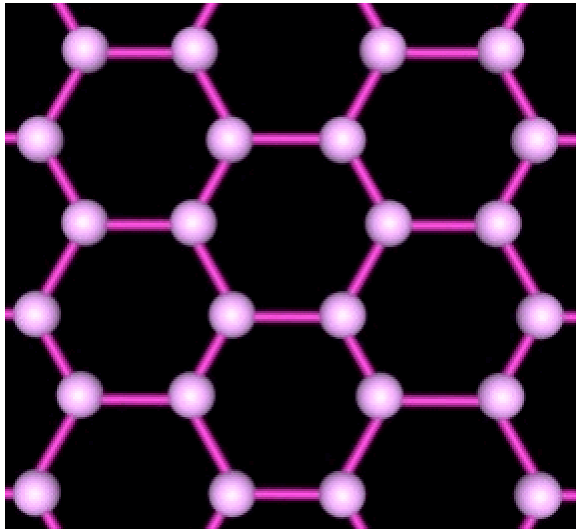




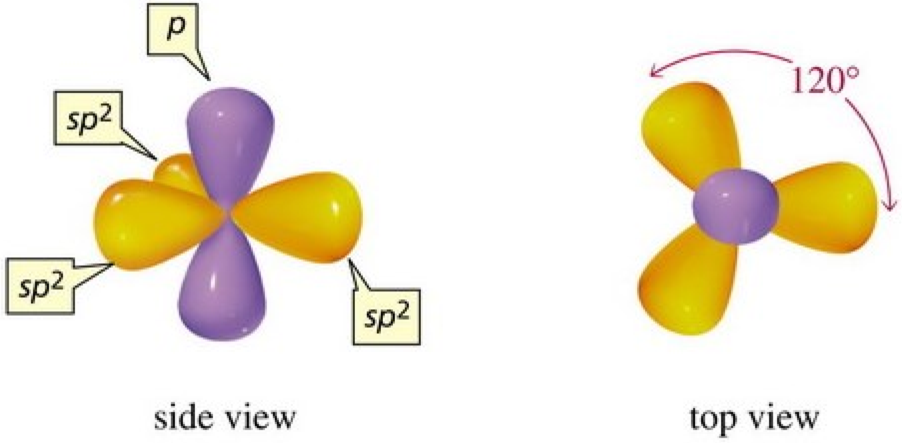


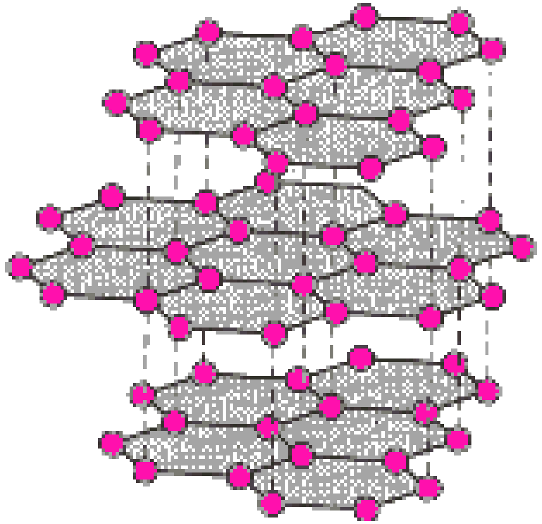
https://socratic.org/questions/how-does-sp2-hybridized-carbon-differ-from-sp3https://www.projectorreviews.com/terms/dlp/
http://www.dianerdiamonds.com/diamond_info/diamond_world_data

Carbon – Orbital Hybridisation



- **sp^2**
- 3 sp orbitals pointing to the corners of an equilateral triangle, 1 p orbital perpendicular to the plane of the triangle
- Graphite structure





https://socratic.org/questions/how-does-sp2-hybridized-carbon-differ-from-sp3https://www.projectorreviews.com/terms/dlp/
http://www.dianerdiamonds.com/diamond_info/diamond_world_data

Diamond and Graphite Properties

Diamond

- Insulator
- Hardest material (10 on the Mohs scale)

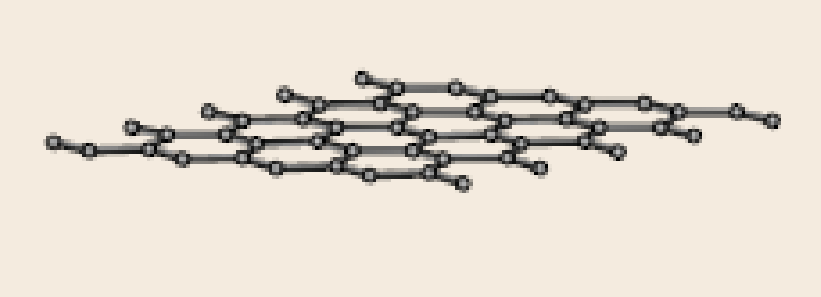
Graphite

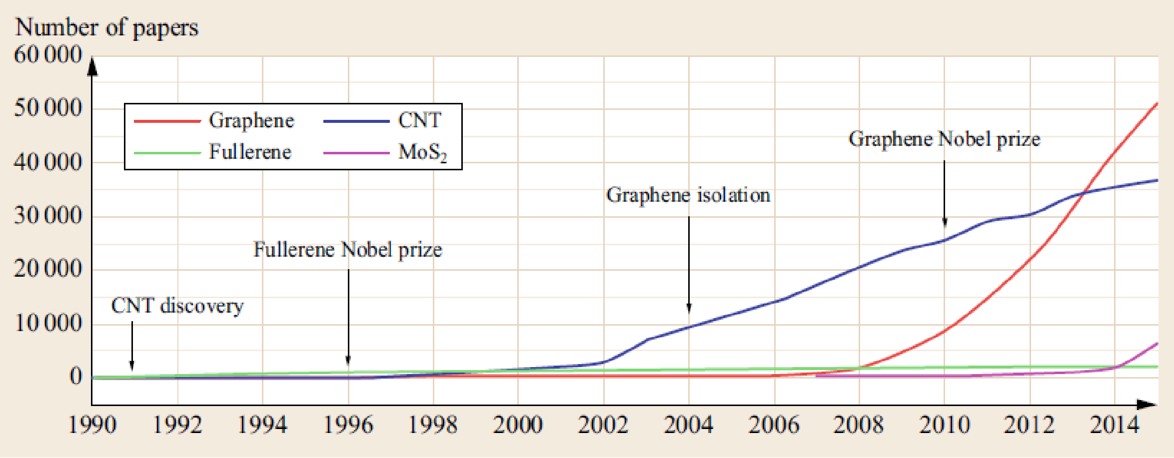
- Excellent electrical conductor
- Soft material (1.5 on the Mohs scale) due to π bonding mediated by 2 p_z orbitals

https://sustainable-nano.com/2014/02/18/the-atomic-difference-between-diamonds-and-graphite/

Graphene

- Single layer of sp^2 graphite
- 2D material – electrons can only move in the plane of the material and not perpendicular to it
- 2004 prepared, 2010 Nobel Prize
- The base material for other carbon allotropes – carbon nanotubes and fullerenes
- Yet discovered last – transformed into another energetically more favorable allotropes during production

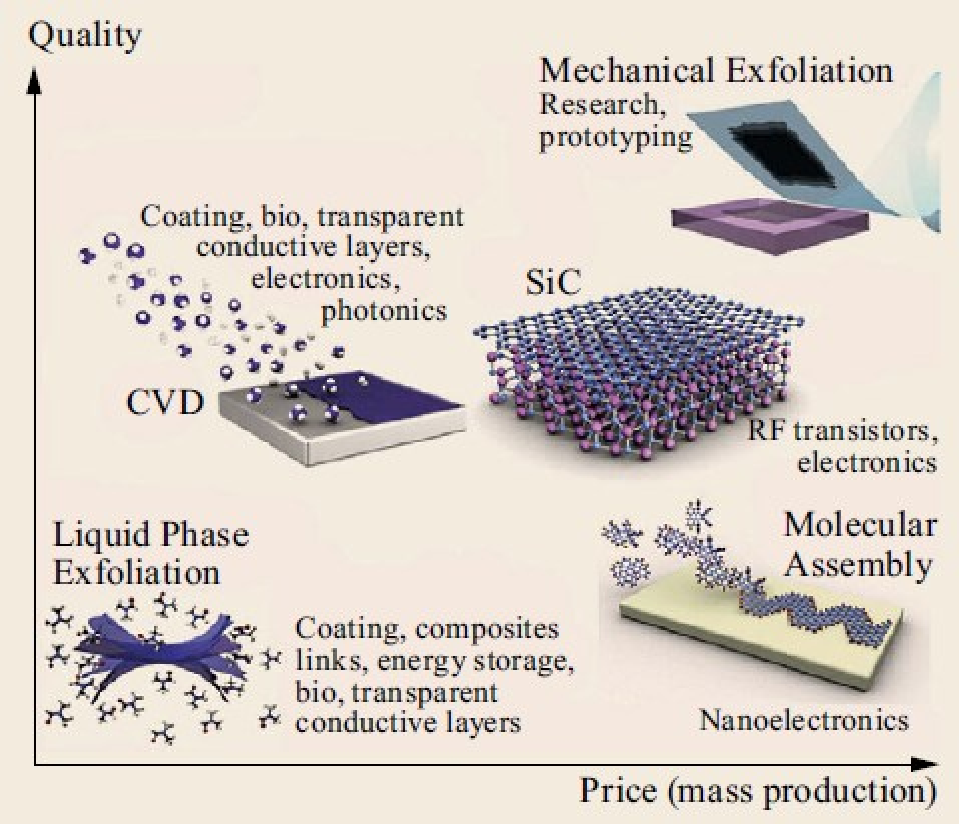




B. Bhushan (Ed.), Springer Handbook of Nanotechnology, 2017

Graphene production

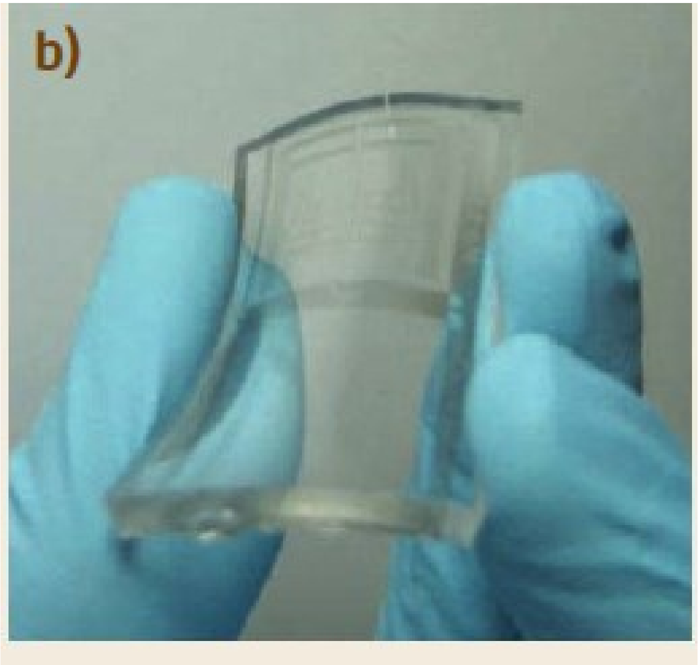
- Micromechanical exfoliation
  - Preparation from graphite using adhesive tape (first preparation method)
- Chemical vapour deposition (CVD)
  - Deposition from hydrocarbon gas on a suitable metal substrate (Ni, Cu)
- Thermal decomposition of carbides
  - High temperature annealing of carbides (> 1000°C) and graphitisation of their surface
- Chemical exfoliation in solvent
  - Production of either pure graphene but only in very small pieces or graphene oxide



B. Bhushan (Ed.), Springer Handbook of Nanotechnology, 2017

Graphene Properties

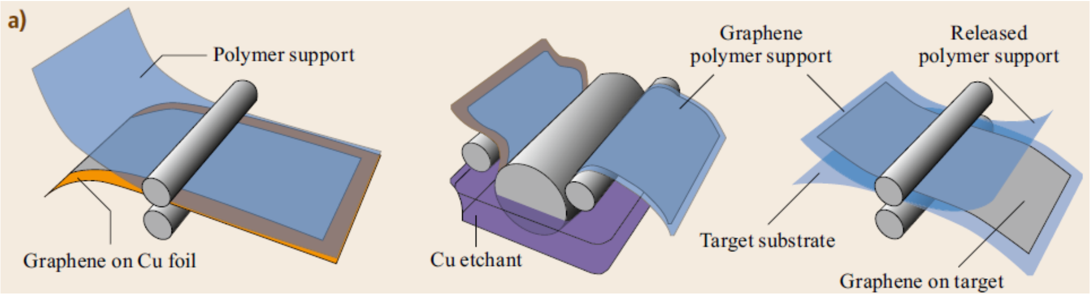
- Mechanical properties measurements have shown a Young's modulus of ~1 TPa, extremely high material stiffness and also high intrinsic strength – the strongest ever measured
- The motion of electrons can be described by the Dirac relativistic equation (Schrödinger equation for 3D materials). Confirmation of quantum electrodynamics – the interaction of electrons and periodic structure - electrons described as massless particles (Dirac fermions) moving at a constant velocity of approximately 10^6 m/s. Klein paradox – they can tunnel through an energy barrier of any height and thickness with probability of 1 – electrons can propagate long distances (microns) in graphene even in the presence of defects or other potentials.
- Light absorption in the visible region is only 2.3% – transparent conductive material
- Chemical activity is entirely surface dependent (every carbon atom that forms graphene is on the surface) – extreme sensitivity.

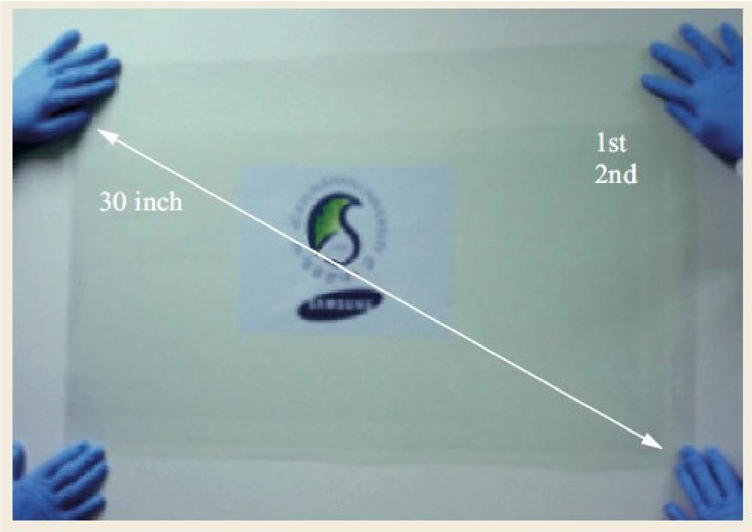


B. Bhushan (Ed.), Springer Handbook of Nanotechnology, 2017

Graphene Applications

- Structural and electrical composites
  - Improving the mechanical properties of materials while increasing their conductivity. Often in the form of thin films (organic photovoltaics, photocatalysis, electrochemical catalysis...)
- Transparent conductive coatings
  - Replacement of current ITO (indium-tin-oxide) coatings
  - Retain their properties even when mechanically stretched by up to several percent – flexible electronics

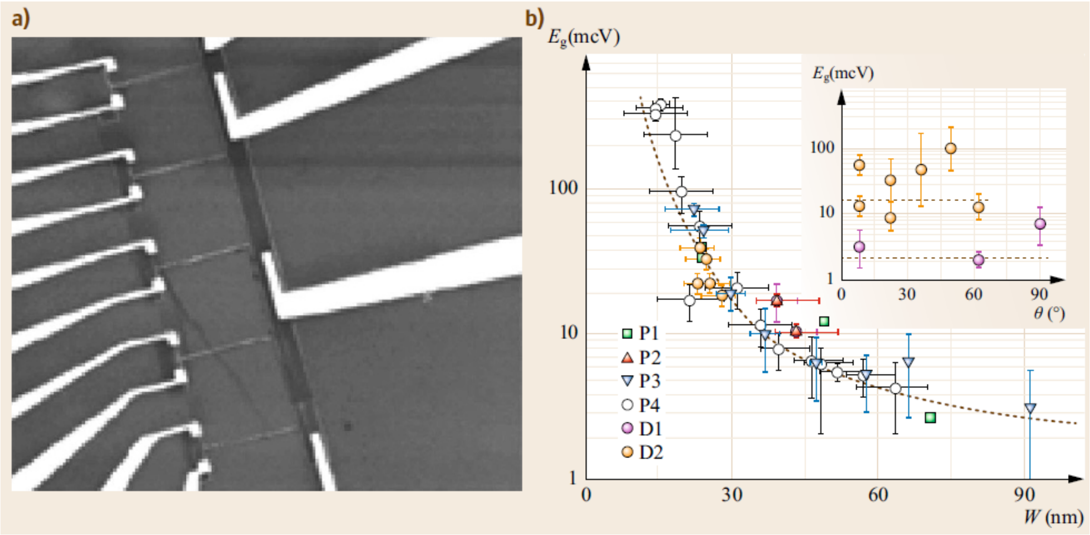


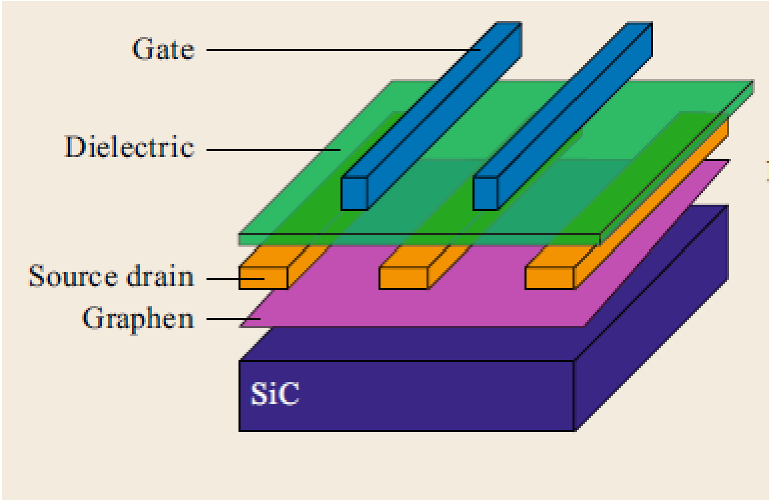


B. Bhushan (Ed.), Springer Handbook of Nanotechnology, 2017

Graphene Applications 2

- Chemical sensors
  - High chemical sensitivity due to large surface area, low electrical noise due to high electron mobility
  - Detection limit in ppb (parts per billion) – detection of warfare chemicals and explosives.
- Electronic components
  - Conductive graphene can be made into a semiconductor – e.g. by limiting the movement of electrons in one direction of the surface (graphene nanoribbons) – forbidden band dependent on the thickness of the ribbon; possibly by an external electric field. Use for FET.
  - Production of graphene quantum dots for SET – Coulomb blockade.



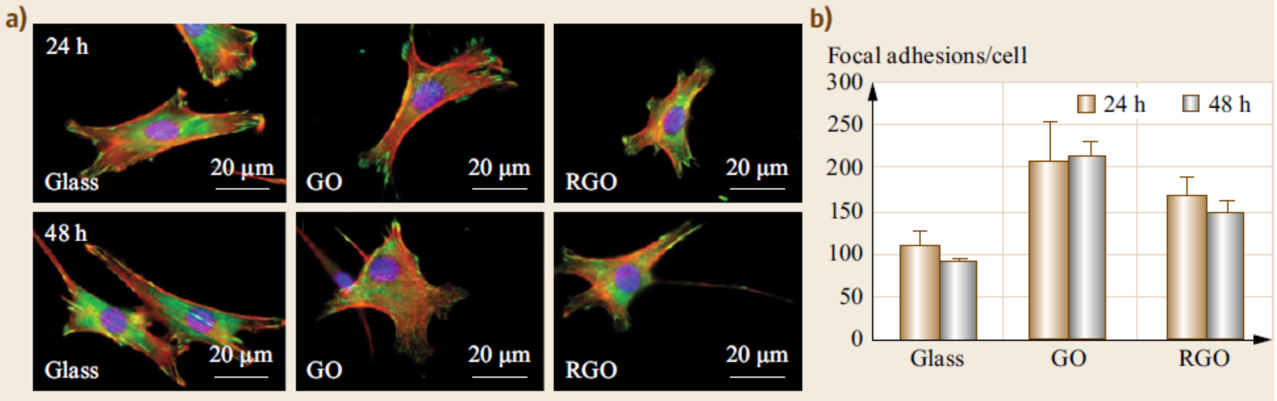


B. Bhushan (Ed.), Springer Handbook of Nanotechnology, 2017

Graphene Applications 3

- Photonics and optoelectronics
  - Graphene has a much larger range of absorbed wavelengths compared to conventional semiconductors. At too large wavelengths (typically > 1 micron), semiconductors are transparent (photons have lower energy than the forbidden band width energy).
  - Combined with low noise, graphene is ideal for photodetectors.

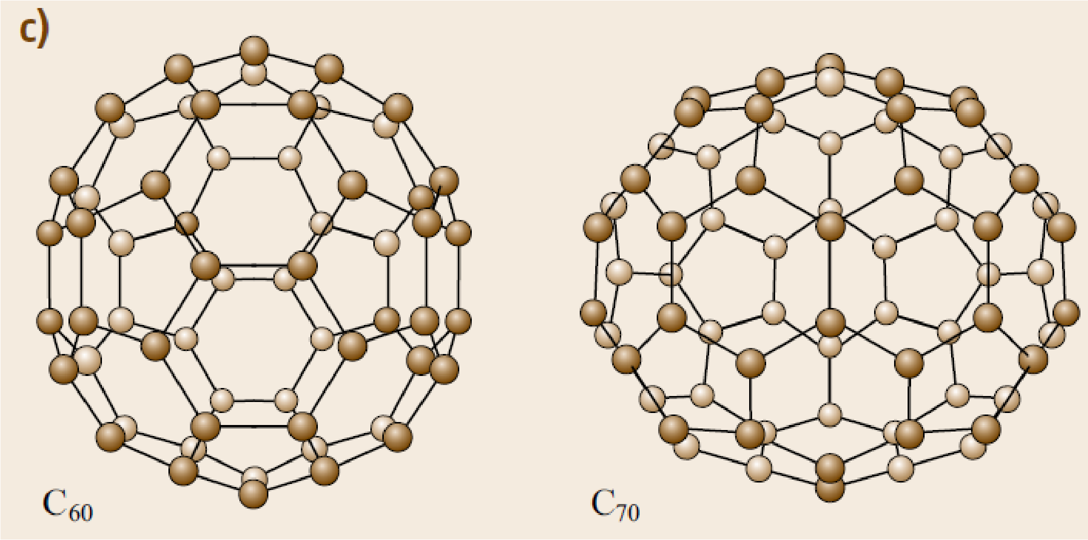
- Biomedical applications
  - Biocompatible material
  - Very small < 100 nm flakes with bound drug can penetrate directly into the cell
  - Photothermal treatment of tumors
  - Cell growth



B. Bhushan (Ed.), Springer Handbook of Nanotechnology, 2017

Fullerenes

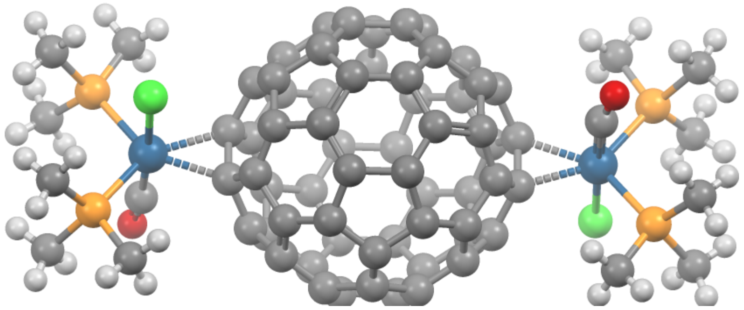
- Spherical molecules (clusters) composed of five- and six-atom rings of carbon atoms.
- 1985 – mass spectroscopy of the products of carbon disk laser sputtering in high vacuum revealed the molecule C_{60}. Separation of a single graphene layer to form a sphere to minimize energy.
- 1996 Nobel Prize in Chemistry



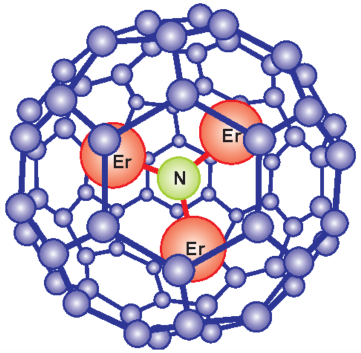
C_{60} – soccer ball
C_{70} – rugby ball

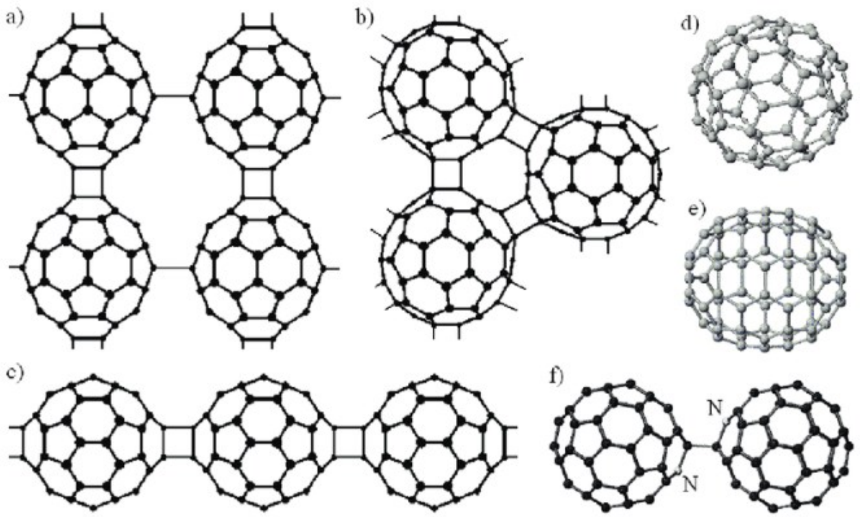
B. Bhushan (Ed.), Springer Handbook of Nanotechnology, 2017

Fullerene Properties



- Extremely mechanically stable (up to 3000 atm)
- Chemically stable, slightly electronegative (can accept several electrons)
- Semiconductors
- Possible modifications:
  - External surface modification (exohedral fullerenes)
  - Placing an atom, molecule, cluster inside (endohedral fullerenes)
  - Arrangement into 2D and 3D structures





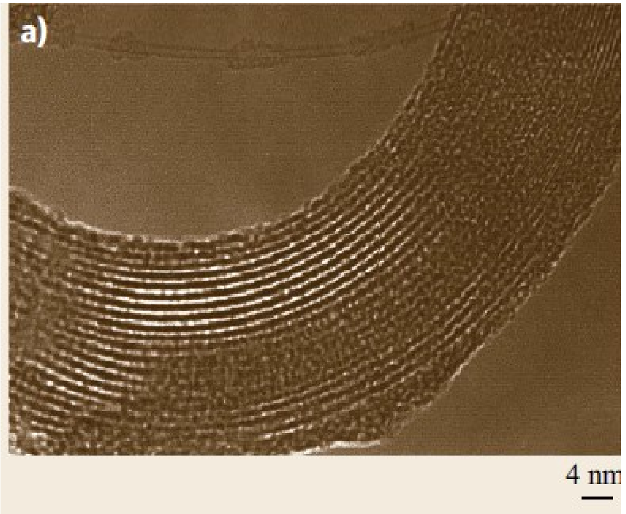
https://en.wikipedia.org/wiki/Transition_metal_fullerene_complex
https://pubmed.ncbi.nlm.nih.gov/20820560/
https://www.researchgate.net/publication/50843622_Surface_electronic_structure_of_fullerides_effects_of_correlation_electron-phonon_coupling_and_polymerization

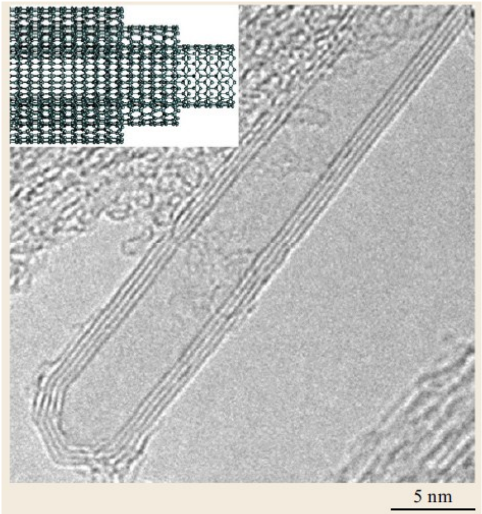
Fullerene Applications

- Semiconductors
  - Forbidden band gap ~ 1.5 eV. Similar to standard semiconductors. For photovoltaics.
- Antioxidants
  - Can absorb electrons, meaning they will bind to free radicals and destroy them.
- Antiviral activity
  - Antioxidant properties and molecular structure lead to antiviral activity – research on HIV treatment
- Photosensitization activity
  - The binding of fullerenes to tumors and their good absorption of EM radiation leads to applications in magnetic resonance imaging of tumors or EM heating therapy.
- Direct drug delivery to targeted sites
  - Use of endohedral fullerenes

Carbon Nanotubes

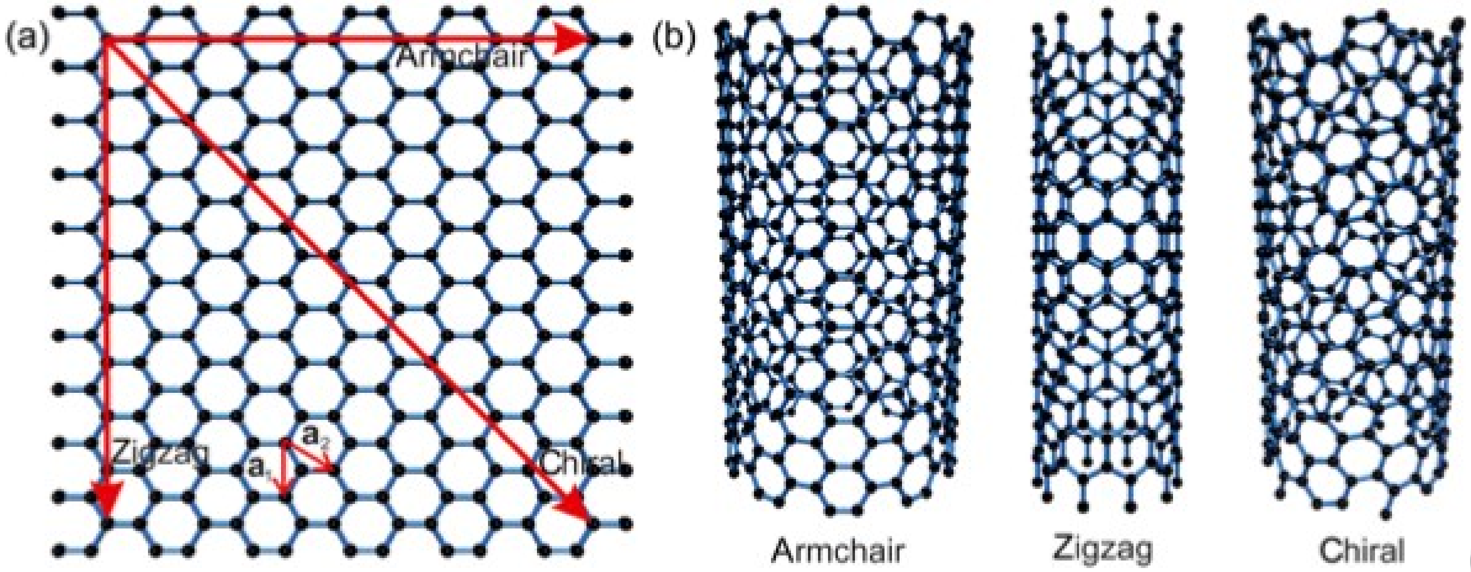
- Discovered in 1991 during observations of carbon black prepared in a low-pressure arc discharge in argon
- There are single wall SWNT (single wall nanotubes) and multiple wall MWNT (multiple walled nanotubes) carbon nanotubes
- Properties depend on the way the graphene layer is rolled



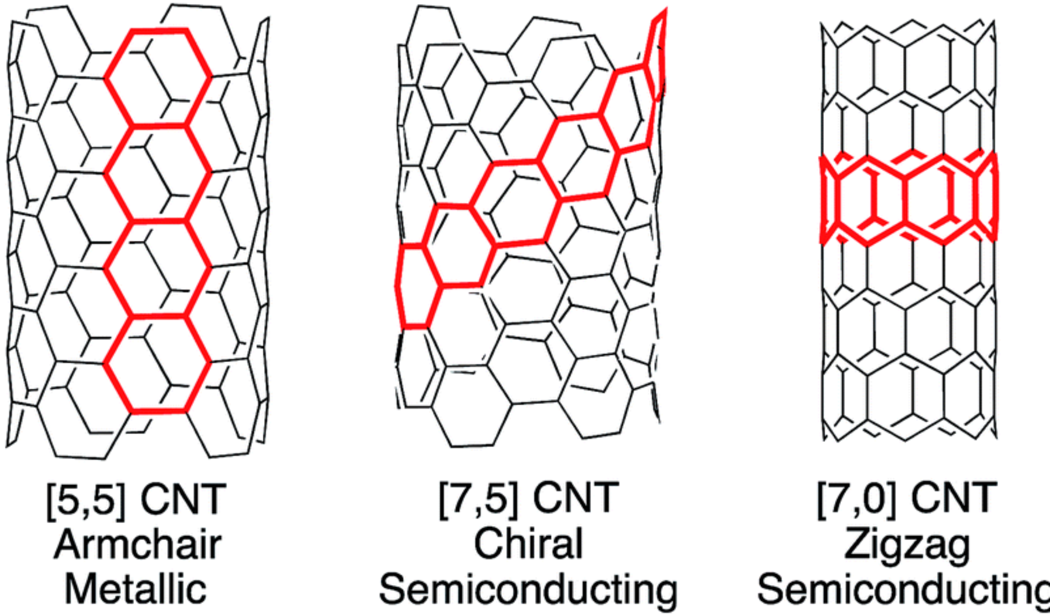


B. Bhushan (Ed.), Springer Handbook of Nanotechnology, 2017

Chirality of the Nanotubes



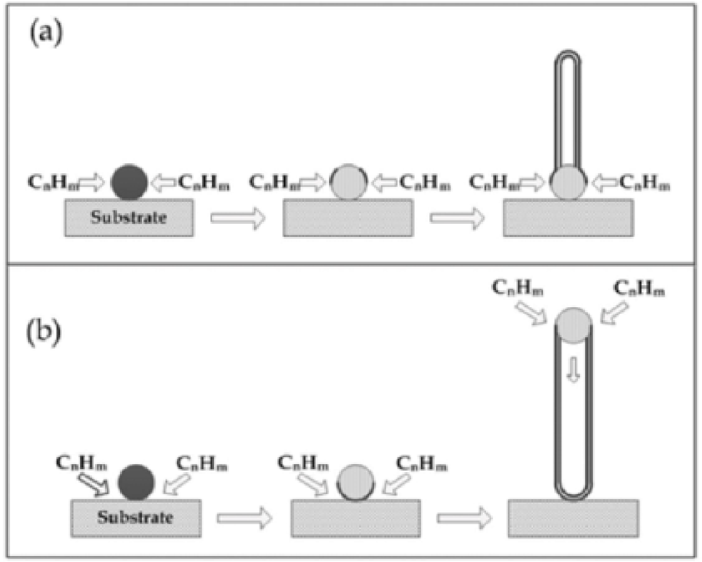
The chiral vector determines the rolling



https://ms.copernicus.org/articles/9/349/2018/
https://pubs.rsc.org/en/content/articlehtml/2016/sc/c5sc04218f

Nanotube Production

- Main methods:
  - Electrode evaporation (doped metals)
  - Laser evaporation of carbon target
  - Chemical vapor deposition (CVD) – plasma or temperature dissociates the gaseous carbon precursor, the atomic carbon then condenses on the substrate.

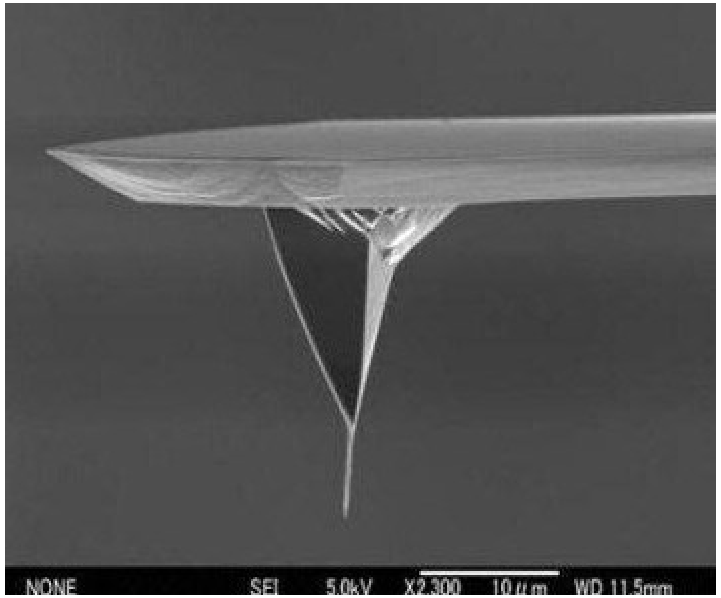


	Increasing temperature … → … and physical state of catalyst		
Catalyst particle size	Solid (crystallized) (1)	Liquid from melting (2)	Liquid from condensing atoms (3)
≲ 3 nm	SWNT	SWNT	–
≳ 3 nm	MWNT (c,h,b) platelet nanofiber	c-MWNT	SWNT
	Nanotube diameter		
	Heterogeneous related to catalyst particle size		Homogeneous (independent of particle size)
	Nanotube/particle		
	One nanotube/particle		Several SWNTs/particle

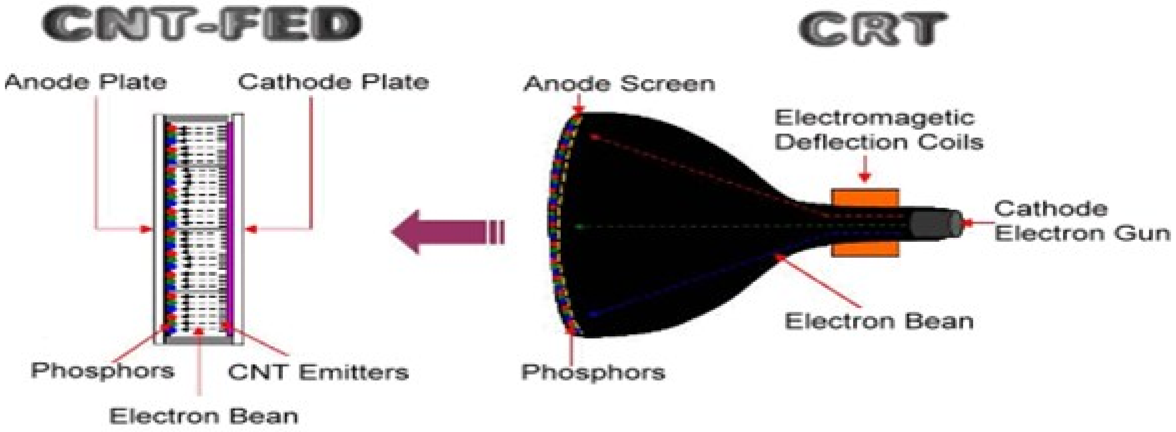
https://www.researchgate.net/publication/316988879_Hydrocarbon_Sources_for_the_Carbon_Nanotubes_Production_by_Chemical_Vapour_Deposition_A_Review
B. Bhushan (Ed.), Springer Handbook of Nanotechnology, 2017

Applications of Carbon Nanotubes

- Tips for probe techniques
  - Suitable as SPM or AFM probe tips due to mechanical and electrical properties



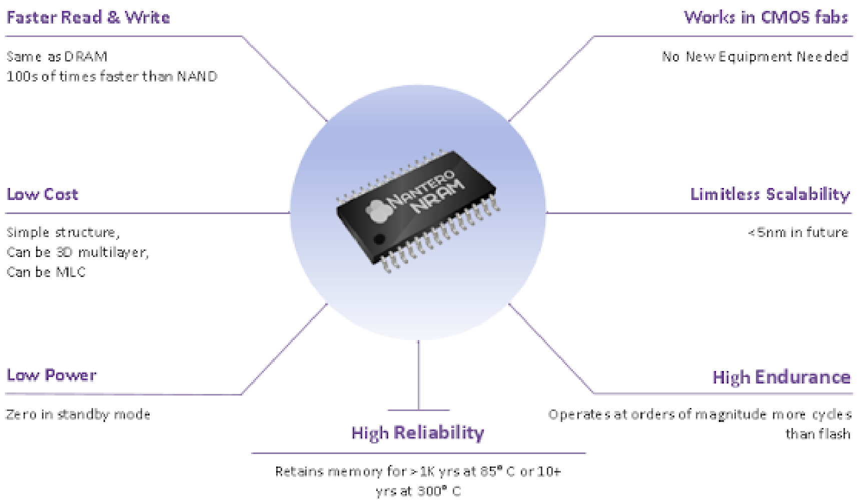
- Electron emitters
  - Highly stable and high yield
  - For displays, X-ray sources or electron microscopes



https://www.indiamart.com/proddetail/carbon-nanotube-based-afm-probe-14893761048.html
https://electronicsmail.wordpress.com/2012/10/09/52/

Applications of Carbon Nanotubes 2

- Flexible Touch-Screen Displays
  - even in small quantities, CNT significantly improve the conductivity of polymers – composites
- Voltage-independent (non-volatile) RAM memories



https://www.nextbigfuture.com/2016/08/carbon-nanotube-nonvolatile-nram-memory.html

- Light absorbers
  - "Carpet" structure – Ventablack
- Mechanical reinforcement of composites
- Anodes for Li-ion batteries
  - Increased capacity over graphite anode (~ 50% of Li-ion batteries for mobile phones and laptops already contain nanotubes as an additive)
  - Chemical sensors

Conclusion

- Diamond x graphite – hybridization
- Graphene – 2D structure
- Fullerenes – spherical molecules
- Carbon nanotubes